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Hillert and Sundman[1] proposed a general model for solute drag on moving grain and interphase boundaries that, along with their subsequent solidification model[2], set the stage for work that followed and gave us a unified picture of the solute drag phenomenon. It followed theoretical treatments of dilute solute drag on grain boundary migration[3,4], and developed in parallel with theoretical treatments of solute drag focused specifically on diffuse, coherent interfaces[5,6].

Hillert and Sundman presented a general expression, applicable to a diffuse interface in a binary alloy comprised of solvent ("A") and solute ("B"), for the force P_B that the solute exerts upon a unit area of interface for an arbitrary profile of solute adsorption free energy. In one of its equivalent forms they wrote it as

$$P_B = -\frac{1}{v}\int_{-\infty}^{\infty} J_B(y)\bullet\frac{d}{dy}\left(G_B(y)-G_A(y)\right)dy \ , \qquad (12a)$$

where v is the interface velocity, J_B is the interdiffusion flux of B relative to A, y is the spatial coordinate in the direction normal to the interface, and G_B and G_A are the chemical potentials of B and A, respectively.

They presented a model for the profile across the interface of the standard free energy of adsorption, ${}^0G_B - {}^0G_A$, that can be applied broadly to a wide variety of intergrain and interphase boundaries. They advanced the correspondence between force per unit area of interface and the dissipation of free energy per mole of material transformed, ΔG_m. They showed how the free energy dissipation rate varies from zone to zone across an interface, depending on y-dependent profiles of ${}^0G_B - {}^0G_A$ and of the interdiffusivity. And they unified the previous pictures of solute drag under this single framework.

Hillert and Sundman proposed an interdiffusivity profile $D(y)$ that varies exponentially with position, i.e. log D linear in y. I believe this profile to be the key to understanding when solute drag effects are substantial or negligible, as discussed below.

The Hillert-Sundman model inspired, in works reviewed by Hillert[7], the generalization of the solute drag treatment to include the force P_{TOT} due to both solute and solvent on the interface. This force can be written[8]

$$P_{TOT} = -\frac{\Delta G_m}{V_m} + \frac{1}{v}\int_0^{\delta} J_B(y)\bullet\frac{d}{dy}\left(G_B(y)-G_A(y)\right)dy \ , \qquad (31)$$

where the limits of integration are the boundaries of the interface region. This "dissipation integral" represents the free energy dissipated by interdiffusion within the interface.

The question has arisen, "how is the interface velocity determined by these forces?" Our experiments[9] in rapid solidification, in which we measured an interface velocity-undercooling function in Si-As alloys with virtually the same slope as in pure Si, are consistent with $v \propto \Delta G_m$. Although there is disagreement on whether $v \propto \Delta G_m$ is permissible based on

theoretical considerations[7,9,10], I think everyone agrees that $v \propto P_{TOT}$ with the dissipation integral on the r.h.s of (31) being negligible for solidification is a plausible explanation of the solidification experiments.

This is currently the only plausible qualitative explanation of which I am aware of the observations that solute drag effects are significant in the migration of grain[11] and anti-phase[6] boundaries but negligible in solidification. Let us see how this explanation[9] arises naturally out of the Hillert-Sundman interface model of an exponentially varying interdiffusivity within an interphase boundary between two phases with vastly different interdiffusivities. In steady-state solidification the first factor in the dissipation integral in (31), J_B, is the interdiffusion flux; the second factor, $\frac{d}{dy}\left(G_B - G_A\right)$, is the thermodynamic driving force for interdiffusion. When either factor approaches zero, dissipation is insignificant. A steep interdiffusivity gradient implies a narrow dissipative zone within a moving interface. In the region of the interface between the dissipative zone and the solid, the mobility is so low that the interdiffusion flux is negligible and the first factor kills the integrand. On the other side, between the dissipative zone and the liquid, the mobility is so high that chemical potential gradients are negligible and the second factor kills the integrand. The steeper the gradient in log D, the narrower the dissipative zone and the smaller is the contribution of the dissipation integral to the r.h.s. of (31). These effects have been worked out quantitatively for the Hillert-Sundman model for solidification of Si-As[9].

For grain and anti-phase boundaries, two effects within the Hillert-Sundman model seem to be responsible for the observation of significant solute drag effects. First, the mobility for interdiffusion may not vary across the interface as markedly as for the crystal/melt interface, thereby leading to a wider dissipative zone than for the crystal/melt interface. This is likely to be the case for anti-phase boundaries. Second, the driving free energy for the transformation, ΔG_m, may be so small that the dissipation integral, though small itself, is not negligible by comparison. This is likely to be the case for both grain and anti-phase boundaries.

I am grateful to Professor Hillert for the pleasant and stimulating discussions that we have had on the subject of solidification and for his profound influence on my thinking about phase transformations, and I commend him on this celebratory occasion.

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